Analysis of Copper by Spark Discharge in Argon Optical Emission Spectrometry (SDAR-OES)

1 Introduction

The concentrations of selected elements in copper serve to chemically characterize it. The elements analyzed in copper can occur as impurities though intentional additions are also made to create alloys. Usually, the impurities are specified not to exceed some maximum level which depends on the copper grade. Below this threshold, significant variation is permissible. Such variation provides a potential means of differentiating among different sources and/or manufacturing processes of copper.

2 Scope

This document applies to personnel using the associated instrument(s)/equipment in support of metallurgy examinations. This procedure provides the examiner with a method for determining the concentrations of several elements, if present above the limits of quantitation (LOQ), in relatively pure copper. These elements include Zn, Sn, Mn, Pb, P, Ni, Mg, Cr, Co, Fe, Ag, Te, As, Sb, Cd, Bi, Al, S, Ti, Se, Si, and O. Extension of the procedure to other elements is possible if additional validation is completed. Operation of the SDAR-OES instrument will follow procedures defined in the current revision of Chemistry Unit (CU) Metallurgy standard operating procedure (SOP) *Compositional Analysis by Spark Discharge in Argon Optical Emission Spectroscopy (SDAR-OES)* and the specific parameters described below.

3 Principle

Compositional analysis of copper by SDAR-OES requires using the predetermined spark sequence to generate characteristic light emissions from the elements present in the specimen. Quantitative determination of individual elemental concentrations is achieved by comparison of measured emission intensities to the manufacturer determined calibration curves resident on the instrument's computer system. The analysis is verified by demonstrating adequate performance on reference materials with similar composition to the evidentiary items.

4 Specimens

This procedure can be used for the analysis of copper sheets, plates, bars, pipes and any other object having sufficiently large physical dimensions. Generally, specimens must be large enough to cover the 13mm diameter analysis area to permit their examination by the method

outlined here. Any specimen that completely covers the opening in the spark source stand is of adequate size.

5 Equipment/Materials/Reagents

a. SpectroLab LAV M10 spectrometer

b. Spectro RH 18/30 optic re-profiling standard

c. Spectro standardization materials: RC 11/4, RC 12/12, and RC 14/20

d. Lathe, bench-top or other

e. Carbide or diamond-tipped cutting tool for lathe dedicated for use on copper

f. High purity argon

g. One or more copper-based certified reference material(s) (CRMs)

h. Additional reference materials as needed

i. Spark stand insert (waveguide), tungsten electrode and wire brush dedicated to copper alloys

j. Vacuum cleaner with precision nozzle attachment

k. Lint-free wipes

6 Standards and Controls

A re-profiling standard is provided by the instrument manufacturer. The standardization materials used in this procedure are specific to the copper alloy class and are specified in the Equipment/Materials/Reagents section. Appropriate CRMs are selected by the operator to verify the standardization of the SDAR-OES instrument over the ranges applicable to the alloy being analyzed. Additional reference materials may be used to further demonstrate instrument performance on a specific element within a similar matrix.

7 Sampling

If an item contains multiple visually indistinguishable objects that are suitable for compositional analysis, a subset may be selected following the procedures for selection, documentation, and reporting detailed in *Examinations for Association and Origin.*

8 Procedure

8.1 Prepare Specimens

Specimens measured by SDAR-OES must be flat and debris-free over the entire analysis region. Prepare the specimen by mounting the it in a lathe and machining the surface to be analyzed to produce a bright finish. To prevent re-oxidation of the surface prior to analysis, specimens should be tested within a short time (several hours) after machining. If significant time elapses, the specimen should be re-machined. This is especially important for oxygen measurement, in which case the specimen should be tested immediately (within one hour) after machining.

8.2 Perform Analysis

Copper analysis uses the "Cu-10 method" that resides on the SpectroLab LAV M10 spectrometer. Follow the procedures detailed in *Compositional Analysis by Spark Discharge in Argon Optical Emission Spectroscopy (SDAR-OES)* to clean, re-profile, and standardize the instrument using the appropriate stage, spark source components and standardization materials. Select CRMs and, if needed, additional reference materials, that contain concentrations of elements of interest that appropriately bound the concentrations present in evidentiary specimens.

9 Instrumental Conditions

The instrumental conditions (i.e., argon flow rate, spark voltage, spark duration, and spark sequence) are set by the instrument manufacturer and are not normally modified by FBI Laboratory personnel. If service of the instrument requires modification of these parameters, the verification sequence will be performed to demonstrate adequate performance on CRMs.

10 Decision Criteria

In general, it is expected that the mean concentration values determined by the instrument on a given CRM will be within the range of values indicated on the certificate of analysis. If a measured element fails to give adequate agreement with the certified value, the instrument can either be re-standardized to improve the agreement or, if the value is not critical, (e.g., determining nominal product characteristics) it may be regarded as qualitative.

The process used to compare data from objects thought to share a common origin is detailed in *Compositional Analysis by Spark Discharge in Argon Optical Emission Spectroscopy (SDAR-OES).*

11 Calculations

11.1 Quantitative Analysis

The measured emission intensity of each element of interest is compared to the emission intensity of a selected matrix line and the system calibration curves. This data is used to determine the weight percentage of each of the elements present. Quantitation of the data is performed automatically by the system program and is not directly controlled by the user.

11.2 Comparative Analysis

Where quantitative data from two specimens are being compared, a pooled, two-tailed, Student's t-test statistic of the sample means is typically used for the comparison as described in *Compositional Analysis by Spark Discharge in Argon Optical Emission Spectroscopy (SDAR-OES)*.

12 Measurement Uncertainty

Quantitative data from this procedure are generally used for comparative purposes as detailed in *Compositional Analysis by Spark Discharge in Argon Optical Emission Spectroscopy (SDAR-OES.*

In the event that it is necessary to estimate the measurement uncertainty of an instrumental result, it will be done in accord with the *Chemistry Unit Procedures for Estimating Measurement Uncertainty*.

13 Limitations

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14 Safety

Wear safety glasses when machining specimens and cleaning and operating the SDAR-OES instrument to prevent eye injury. Additionally, wear lab coat and gloves when cleaning the instrument and changing the air filter.

15 References

Thomsen, V. B. E., *Modern Spectrochemical Analysis of Metals - An Introduction for Users of Arc/Spark Instrumentation*, ASM International 1996

Slickers, K., *Automatic Atomic-Emission-Spectroscopy, 2nd Ed.*, Bruhlsche Universitatsdruckerei, Germany 1993

Milton, J. S. and Arnold, J. C., *Introduction to Probability and Statistics - Principles and Applications for Engineering and Computer Sciences, Fourth Edition*, McGraw-Hill Higher Education 2003

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Examinations for Association or Origin, Metallurgy Manual 100, Chemistry Unit, latest revision

FBI Laboratory Quality Assurance Manual, Federal Bureau of Investigation, Laboratory Division, latest revision

Compositional Analysis by Spark Discharge in Argon Optical Emission Spectroscopy (SDAR-OES), Metallurgy Manual 400, Chemistry Unit, latest revision

Rev. #	Issue Date	History
4	03/02/2018	Renumbered Metallurgy SOP Manual documents. This document was formerly Metal 21 and is now designated Metal 403. Added personnel to section 2. Removed information that has been relocated to Metal 400: *Compositional Analysis by Spark Discharge in Argon Optical Emission Spectroscopy (SDAR-OES)* throughout, renumbered sections and designated dependence on this document. Made minor editorial corrections throughout document. Added requirement for sampling plan retention in section 7. Added CRM verification in section 3. Changed units in LOQ table in section 13. Augmented section 14. Added additional references to section 15.
5	07/15/2021	Updated Scope. Minor grammatical changes. Changed "sample" to "specimen", "object", or "material" as appropriate. Clarified Surface Preparation, Instrumental Conditions, Decision Criteria, and Limitations sections. Added reference to *Examinations for Association or Origin* in Sampling and References sections. Changed measurement uncertainty section to refer to *Compositional Analysis by Spark Discharge in Argon Optical Emission Spectroscopy (SDAR-OES)*. Added source of data to Table 1 title and reformatted data.

Approval

Redact - Signatures on File

Metallurgy Technical Leader: Date: 07/14/2021

Chemistry Unit Chief: Date: 07/14/2021